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Simultaneous Multi-Element Determination of Bismuth (Bi), Antimony (Sb), and Selenium (Se)

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ABSTRACT

A simple method was developed for the direct and simultaneous determination of Bi, Sb, and Se in biological samples by a multi-element graphite furnace atomic absorption spectrometer (Perkin-Elmer SIMAA 6000). Two types of modifiers; Pd+Mg mixture modifier and Ir as a permanent modifier, were used. A standard reference material (SRM) of Seronorm™ Trace Elements in urine was used to develop the optimum conditions for multi-element determination. The optimum conditions for the analysis of urine sample are pyrolysis at 1000°C and atomization at 1900°C (using Pd+Mg modifier) and pyrolysis at 800°C and atomization at 1900°C (using Ir-permanent modifier). Numbers of reference standard materials were used to confirm the accuracy of the method. The found values were within 99.6-109 % for Bi, 95-105.5 % for Sb, and 96.9-106.9 % for Se of the certified values. The detection limits were 0.82-1.9 µg.l^{-1} for Bi, 0.67-1.7 µg.l^{-1} for Sb, and 0.92-2.4 µg.l^{-1} for Se. The relative standard deviations (R.S.D.s) for the analysis of SRM were 8.9 % for Bi, 5.9 % for Sb, and 9.4 % for Se. Analysis of standard reference materials were in good agreement with certified values.

Keywords: Simultaneous multi-element, Graphite Furnace AAS, Bismuth, Antimony, Selenium

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INTRODUCTION

Graphite furnace atomic absorption spectrometry (GFAAS), also known as electrothermal atomic absorption spectroscopy (ETAAS), is a suitable and widely used technique to determine elements at trace levels [1-7]. For many elements, GFAAS offers detection limits superior to those of inductively coupled plasma atomic emission spectroscopy (ICP-AES). Moreover, sample consumption in GFAAS is much lower than of ICP-AES meaning that experiments can be conducted on a microscale level, consuming lower quantities of expensive standards and generally lesser amounts of waste [8]. GFAAS is particularly advantageous in the analysis of complex samples. The removal of solvent, pyrolysis, and atomization can be carried out in discrete steps permitting, particularly with the aid of chemical modification, selective removal of matrix components. Thus freedom from interferences can be attained in many cases.

Compared with atomic emission spectroscopic technique, GFAAS suffers from the very beginning from the fact that it has been developed as a single-element technique. The multi-element determination is possible in sequential manner only. Thus, due to the usual length of the electrothermal programs (sometimes several minutes), its main drawback is a time-consuming analysis. Another main disadvantage of GFAAS over emission methods is the poor dynamic range of about two orders of magnitude only (up to 10 in some ICP-AES realizations).

Since 1960s a variety of multi-element AAS techniques have been developed and performed. Both line and continuous sources have been used, various optical dispersion systems, and several types of detectors have been tested [9-25]. In recent years, owing to the availability of several commercial multi-element GFAAS instruments (four types at least), the analytical potential of GFAAS has increased [26].

The development and evaluation of; a fast, reliable, and comparable (in terms of detection limits and sensitivity) to the single-element analytical methodology for the simultaneous multi-element determination of bismuth, antimony, and selenium in biological samples by SIMMA 6000 instrument is the aim of this work.

Instrumentation and Reagents

Measurements were performed with a SIMAA 6000 system (Simultaneous Multi-element Atomic Absorption Spectrometer) equipped with a longitudinal Zeeman-effect background correction, an AS-72 autosampler, an Echelle optical arrangement, and a Solid-state detector (Perkin-Elmer GmbH, Bodenseewerk, D-88647 Überlingen). A transversely heated graphite atomizer (THGA) tubes with an integrated platform were used throughout this work. The whole system was controlled by means of AA Winlab^{TM} control software running under Microsoft Windows^{TM}. High-purity argon (99.998 %, Air Liquid Deutschland GmbH) was used as the purge gas. The rate of flow of the inert gas was 250 ml.min^{-1}. This flow was stopped during atomization. The lamps used were EDLs from Perkin-Elmer and the wavelengths for each lamp were: Bi 223.1 nm, Sb 217.6 nm, Se 196.0 nm. The integrated absorbance of the atomic absorption signal was used for the determination. The integrated absorbance of the atomic absorption signal was used for the determination.

All solutions were prepared with high purity de-ionized water (18.2 MΩ) obtained from a Milli-Q water purification system (Millipore GmbH, Schwalbach, Deutschland). Analytical reagent-grade HNO_3 65% (KMF Laborchemie Handels GmbH, Lohmer, Deutschland) was purified by sub-boiling distillation. High purity standard reference solutions (1.000 g.l^{-1}) from Bernd Kraft GmbH, Duisburg-Deutschland, were used to prepare the analytical stock solutions which are kept in a refrigerator. The reference solutions for calibration and determination were prepared daily by appropriate dilution of the stock solution with 0.2% HNO_3.

The chemical modifier solutions used were $Pd(NO_3)_2$, $Mg(NO_3)_2$, and Ir. In each measurement, 20 µl sample or standard solution, 5 µl 1.000 g.l^{-1} Pd solution, and 3 µl 1.000 g.l^{-1} $Mg(NO_3)_2$ solution were injected into the graphite tube at 20^{o}C. In the case of the multi-element determination by using a permanent modifier, the tubes were prepared by pipetting 20 µl of a 1.000 g.l^{-1} of Ir, as chloride, and submitting the tube to the temperature program shown in Table 1 [27]. The entire procedure, that is, the pipetting and heating, was repeated 25 times.

All glassware, micropipette tips, autosampler cups, and polypropylene containers were acid washed with 10% (v/v) HNO_3 for 24 hr. and thoroughly rinsed five times with distilled water before use. All solutions and samples were daily prepared in 0.2% (v/v) HNO_3.

Table 1. Temperature Program for the Metal Coating

Step	Temperature (^{o}C)	Ramp (s)	Hold (s)	Ar flow rate (ml.min^{-1})
1	90	5	30	250
2	140	5	30	250
3	1000	10	10	250
4	2000	0	5	0
5	20	1	10	250

The accuracy of the methods was confirmed by analyzing different certified reference materials [28]. The certified reference materials were shown in Table 2.

Table 2. Certified Reference Materials

Certified Material	LOT	Source
Trace Element Urine Sample	0511545	Seronorm
Lyphocheck Urine Metals Control-Level 1	69061	BIO-RAD
Bovine Liver	NIST-SRM 1577b	National Institute of Standards and Technology
Pig Kidney	BCR-CRM 186	Institute for Reference Materials and Measurements
Pork Liver	GBW 08551	National Research Centre for Certified Reference Materials
Tea	GBW 08505	National Research Centre for Certified Reference Materials

Trace Elements Urine Sample (Seronorm 0511545)
Exactly 5 ml de-ionized water was added to the sample and let it stand for 30 min, and then transfer it to a plastic tube. The sample was then kept in a refrigerator at -20^{o}C for later use. Before use, the sample was diluted 1:4 with 0.2% HNO_3.

Lyphocheck Urine Metals Control–Level 1 from BIO-RAD (69061)
The same procedure was applied as Seronorm sample except that, 25 ml de-ionized water was added and the sample was diluted 1:1 before use.

Bovine Liver, Pig Kidney, and Pork Liver
The samples were digested as described by Ronald Treble [29]. Firstly, the samples were dried at 80^{o}C for 4 hr. and stored in desiccators before use. 0.5069 g (GBW 08551), 0.5218 g (BCR-CRM 186), and 0.5129 g (NIST-SRM 1577b) dried samples were allowed to digest in 5 ml concentrated distilled HNO_3 for a period of 72 hr. at room temperature. The digested/acidified samples were transferred into 50 ml volumetric flask and diluted to the mark with de-ionized water. Before use, each sample was diluted as required.

Tea Sample
The sample was digested as described by Yin Ming [30]. The sample firstly was dried at 80^{o}C for 4 hr. in a clean oven and stored in desiccators before use. A sample portion of 1.0217 g was weighed into a beaker and moistened with pure water. 10 ml HNO_3 and 2 ml $HClO_4$ were added in sequence. After standing overnight, the sample was evaporated to nearly dry on a hotplate at 200^{o}C. The resulting residue was treated with 0.5 ml concentrated HNO_3 and some water, and then heated gently for 5 min. till the solution turned clear. This solution was rinsed into a 50 ml volumetric flask and diluted to the mark with de-ionized water. The sample was diluted as required before use.

RESULTS AND DISCUSSION

We have firstly optimized the parameters for the single-element determinations. These conditions include the pyrolysis and atomization temperatures which have been determined with modifiers. Two types of modifiers have been used; the Pd+Mg mixture modifier and Ir-permanent modifier. From the optimized parameters, the sensitivities, the characteristic masses, and the detection limits have been determined. Secondly, the compromised conditions for the multi-element determinations have been determined and then used to determine the sensitivities, the characteristic masses, and the detection limits. To test the accuracy of our methods, the compromised conditions have been used to analyze number of certified reference materials. Also the effect of strong matrix on these compromised conditions has been studied by using urine reference material from Seronorm which has been diluted because of the high concentration of the elements.

Single-element mode optimization
When ETAAS is used for single-element determination, all experimental and instrumental parameters are optimized for only one analyte. Consequently, the best optimized pyrolysis and atomization temperatures are used in the heating program, minimizing condensed and gas-phase interference. The best pyrolysis and atomization temperatures were determined according to the pyrolysis and atomization curves and the absorbance peak for each element. The heating program was summarized in Table 3. The heating program for each element was used to determine the detection limits and the characteristic mass for each element and they were summarized in Table 4.

Table 3. Temperature Program for Determination of Bi, Sb, and Se with different Modifiers

Step	Temperature (^{o}C)	Ramp Time (s)	Hold Time (s)	Gas Flow (ml.min^{-1})
Dry 1	110	1	30	250
Dry 2	130	15	30	250
Pyrolysis	Various[a,b]	10	20	250
Atomization	Various[c,d]	0	5	0
Clean-out	2550	1	4	250

[a] *1100, 1300, 1200^{o}C for Bi, Sb, Se with Pd+Mg modifier and 1100^{o}C for multi-element determination*
[b] *1200, 1400, 1300^{o}C for Bi, Sb, Se with Ir modifier and 1200^{o}C for multi-element determination*
[c] *1800, 1900^{o}C for Bi, (Sb and Se) with Pd+Mg modifier and 1900^{o}C for multi-element determination*
[d] *1900, 2100, 2000^{o}C for Bi, Sb, Se with Ir modifier and 2000^{o}C for multi-element determination*

Table 4. The Characteristic mass and Detection Limits with different Modifiers

Element	LOD ($\mu g.l^{-1}$)				Characteristic mass (pg)			
	Single		Multi		Single		Multi	
	Pd+Mg	Ir	Pd+Mg	Ir	Pd+Mg	Ir	Pd+Mg	Ir
Bi	0.46	0.50	0.82	1.50	67.7	73.3	80	73.3
Sb	0.29	0.63	0.57	1.13	41.9	46.3	41.9	55.0
Se	0.40	0.30	0.86	0.75	58.7	44.0	62.9	44.0

Multi-element mode optimization

In this case, the experimental and instrumental parameters are optimized for all elements in the multi-element mode. The heating program temperature and the chemical modifier must be carefully selected to achieve the best atomization efficiency for all the analytes. In general, the most volatile analyte determines the pyrolysis temperature while the least volatile one determines the atomization temperature.

The main purpose of using chemical modification in ETAAS is to stabilize the elements to a pyrolysis temperature as high as possible in order to remove the sample matrix efficiently in the thermal pre-treatment step hence less interferences are encountered in the final atomization process. However, chemical modification is more frequently applied to the stabilization of elements of high and medium volatility.

The mixture of palladium and magnesium nitrate has been widely used for simultaneous multi-element determinations by SIMAA 6000 [31]. It is claimed as universal chemical modifier due to thermal stability improvement for 21 elements [32]. We have used this mixture as a modifier in our work. The stabilizing effect of this modifier on these elements, which results from the formation of a chemical compound or of an inter-metallic phase and/or from an imbedding effect, is not limited to the pyrolysis step but also increases the atomization temperature. At higher atomization temperatures, the diffusion losses of these elements are higher so that lower integrated absorbances are obtained [32].

The use of permanent chemical modifiers allows increases the graphite tube lifetime, eliminates volatile impurities during the thermal coating process, decreases the detection limits, reduce the total heating cycle time, and minimize the high purity chemical consumption. The use of pre-reduced noble metal permanent modifiers such as Pd, Rh, Ru, Pt, and Ir [33-39], carbide forming elements (W, Zr, Nb, Ta) [40,41], and mixed carbide forming elements (W, Zr) with Ir [42-44] have been applied successfully for trapping of hydride-forming elements in ETAAS. In our study, we have used Ir as a permanent modifier for the simultaneous multi-element determination.

The heating program temperature was summarized in Table 3. Fig. 1 shows the pyrolysis and atomization curves for each element with Pd + Mg modifier. The best pyrolysis temperature for the multi-element determination was 1100^{o}C because the absorption signal for Bi decreased above 1100^{o}C. The atomic signal for Sb was almost constant until 1300^{o}C and then gradually decreased. From the atomization curves, Sb, and Se atomic absorption signals increased with increasing the atomization temperature until 1900^{o}C and then start to decrease. For that reason we have decided to choose 1900^{o}C as the optimum atomization temperature. Fig. 2 shows the pyrolysis and atomization curves for each element with Ir-permanent modifier, the best pyrolysis and atomization temperatures for the multi-element determination were 1200^{o}C and 2000^{o}C. Higher pyrolysis temperatures; compared to that with Pd+Mg modifier, can be used. Also, higher atomization temperatures, especially for Sb, are required and this means more stabilization effect with this modifier will be obtained.The pyrolysis and atomization curves were made using the following concentrations: 100 ppb Bi, 100 ppb Sb, and 100 ppb Se in 0.2% HNO_3. The detection limits and the characteristic mass for each element were determined and summarized in Table 4. The values of the characteristic mass are comparable with those of the single-element determinations. The higher detection limits for multi-element mode in comparison with single-element mode, can be related to the compromised conditions adopted for the simultaneous determination.

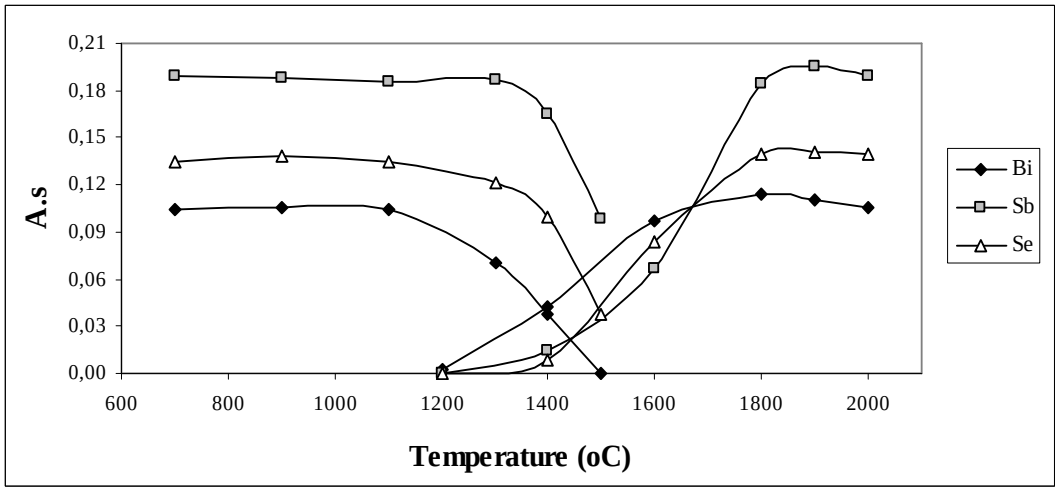

Fig. 1. Pyrolysis and atomization curves of multi-element determination of Bi, Sb, and Se in aqueous solution with Pd+Mg modifier

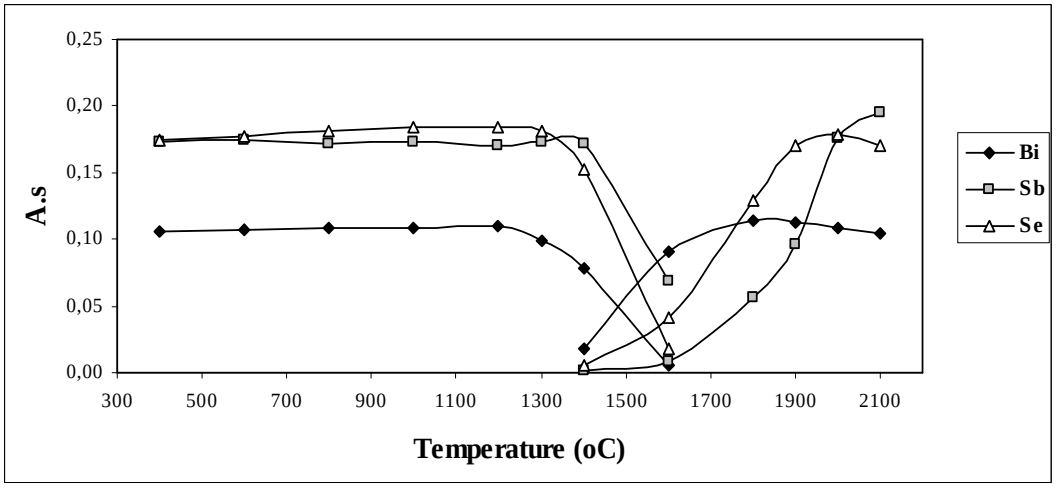

Fig. 2. Pyrolysis and atomization curves of multi-element determination of Bi, Sb, and Se in aqueous solution with Ir-permanent modifier

Study the effect of the matrix

In our work, we have used standard reference urine sample from Seronorm (LOT 0511545) to study the effect of the matrix on the pyrolysis and atomization curves of the simultaneous multi-element determination of our elements. Since the concentrations of most elements in the reference material were high, we have diluted it (1:4), which has also reduced the concentration of the interferences. The resulting temperature program has been used to evaluate the concentrations of the elements in different types of reference materials.

With Pd+Mg Modifier

The diluted reference material (1:4) has been spiked with 80 ppb Bi, 80 ppb Sb, and 80 ppb Se. 20 µl diluted spiked reference material has been injected with 5µg Pd + 3µg $Mg(NO_3)_2$ as a modifier into the atomizer each time during this study. The dependence of Bi, Sb, and Se absorbance on the pyrolysis temperature at 1900^{o}C atomization temperature was studied and shown in Fig 3. For Bi and Se, the atomic signal was almost constant till 1000^{o}C and 1100^{o}C, respectively, then started gradually to decrease. For Sb, the atomic absorption remained almost constant until 1200^{o}C and then gradually decreased. In order to determine all three elements simultaneously, 1000^{o}C was chosen as an optimum pyrolysis temperature. Similarly, the effects of atomization temperature on the atomic absorbance are studied and shown in Figure 3. The effect of the atomization temperature was studied at the pyrolysis of 1000^{o}C. For Bi, the atomic absorption signal increased with increasing atomization temperature and had its maximum at atomization temperature between 1600-1900^{o}C and then started to decrease. Sb and Se atomic absorption signals had their maximum at approximately 1900^{o}C atomization temperature. By taking into account the atomic signal, 1900^{o}C was chosen as an optimum atomization temperature for the simultaneous determination of the

elements. The absorption peaks of the elements at the optimum pyrolysis and atomization temperatures are shown in Figure 4.

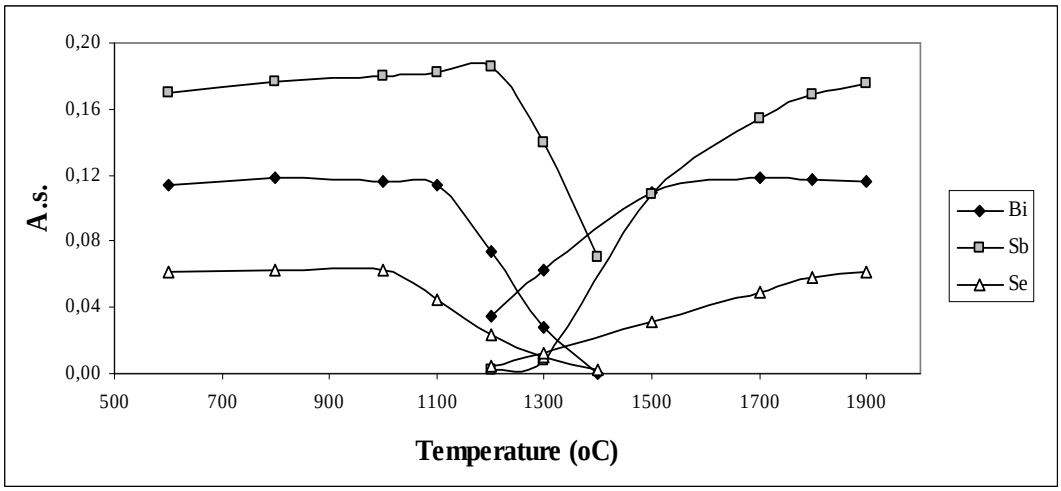

Fig. 3. Pyrolysis and atomization curves of Bi, Sb, and Se in diluted urine sample with Pd+Mg modifier

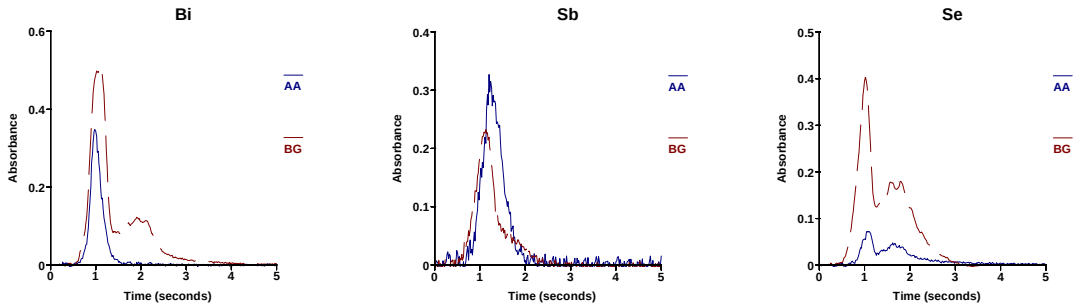

Fig. 4. Peak signals for multi-element determination in diluted urine sample with Pd+Mg modifier

With Ir-Permanent Modifier

The 500µg iridium was thermally deposited on the graphite tube platform and used as permanent modifier. The diluted reference material (1:4) has been spiked with 80 ppb Bi, 80 ppb Sb, and 80 ppb Se. 20 µl diluted spiked reference material has been injected into the atomizer each time during this study. The dependence of Bi, Sb, and Se absorbance on the pyrolysis temperature at 1900^{o}C atomization temperature was studied and shown in Figure 5. For Bi, Se, and Sb, the atomic signal was almost constant till 800, 1000 and 1200^{o}C, respectively, then started gradually to decrease. A decreased in the pyrolysis temperature comparing with the determination of these elements in the aqueous solution (1200, 1300 and 1400^{o}C for Bi, Se, and Sb, respectively) can be seen. C. G. Magalhães et al. [45] found that with iridium applied in solution together with the urine sample, the best pyrolysis temperature was 900^{o}C but the sensitivity was analogous with that obtained using Pd+Mg modifier. They [39] found also with Ir+Rh permanent modifier that the best pyrolysis temperature was 900^{o}C. Using W+Rh permanent modifier, Oliveira et al. [46] reported 400^{o}C as the best pyrolysis temperature for the determination of Cd in urine sample. E. Bulska et al. [47] determined Sb in biological samples using different types of modifiers and fond that iridium stabilized antimony to higher temperature when compared with palladium, but significant decrease in absorbance value of 23% was observed. In order to determine all three elements simultaneously, 800^{o}C was chosen as an optimum pyrolysis temperature. The effect of the atomization temperature was studied at the pyrolysis of 800^{o}C. For Bi, the atomic absorption signal increased with increasing atomization temperature and had its maximum at atomization temperature between 1200-1300^{o}C and then started to decrease. Sb and Se atomic absorption signals had their maximum at approximately 1900^{o}C atomization temperature. For the simultaneous determination of the elements, 1900^{o}C was chosen as an optimum atomization temperature. The signal absorption peaks at the optimum pyrolysis and atomization temperatures are shown in Figure 6.

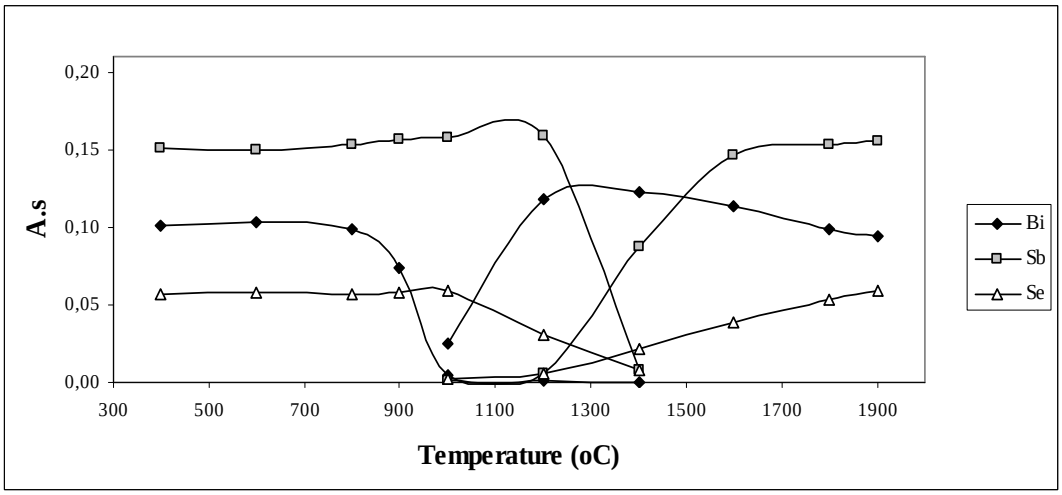

Fig. 5. Pyrolysis and atomization curves of Bi, Sb, and Se in diluted urine sample with Ir modifier

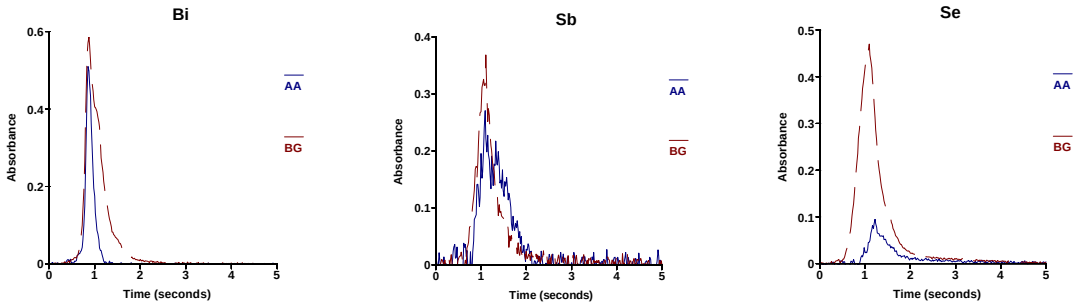

Fig. 6. Peak signals for multi-element determination in diluted urine sample with Ir-permanent modifier

Analysis of Certified Reference Materials

Number of certified reference materials was used to test the simultaneous determination methodologies that we have developed. The optimum pyrolysis and atomization temperatures that have been developed using urine matrix were used to analyze the reference materials. The standard addition curves were used to analyze the reference materials. The peak area of the atomic absorption signal was used for the determination and each experimental value is the average of five determinations. Detection limits were calculated as three times the standard deviation of ten replicate measurements of the blank. Generally, the analyzed values for all elements in all reference materials were within the range of certified values.

Trace Element Urine Sample from Seronorm (0511545)

Two types of modifiers have been used; the mixture of Pd and Mg and Ir as a permanent modifier, in the multi-element determination of bismuth, antimony, and selenium in the urine sample from Seronorm. The sample was diluted (1:4, v/v) with 0.2% HNO_3 and 20µl of the sample was injected for each measurement. 5µl of 1.00 $g.l^{-1}$ Pd and 3µl 1.00 $g.l^{-1}$ $Mg(NO_3)_2$ were injected also with the sample into the graphite tube.

With Pd+Mg modifier

The standard addition curves with good linearity (R^2 = 0.998, 0.9996, and 0.9997 for Bi, Sb, and Se, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified concentrations in Table 5. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 102, 95, and 103.8 % for Bi, Sb, and Se, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 5.

With Ir-permanent modifier

The standard addition curves with good linearity (R^2 = 0.9995, 0.9999, and 0.9994 for Bi, Sb, and Se, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified concentrations in Table 5. The experimentally determined concentrations were in good agreement

with the certified values. The analyzed values were in the range of 109, 105.5, and 100.7 % for Bi, Sb, and Se, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 5.

Lyphochek Urine Metals Control Level 1 from BIO-RAD (69061)

The sample was diluted (1:1, v/v) with 0.2% HNO_3. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 $g.l^{-1}$ $Pd(NO_3)_2$ and 3 µl of 1.00 $g.l^{1}$ $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20°C. No certified value for bismuth; therefore, the sample has spiked with bismuth before the dilution.

The standard addition curves with good linearity (R^2 = 0.9996, 0.9997, and 0.9999 for Bi, Sb, and Se, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified concentrations in Table 5. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 101.7, 102.4, and 106.9% for Bi, Sb, and Se, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 5.

Bovine Liver from National Institute of Standards and Technology (NIST-SRM 1577b)

The sample was used without dilution. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 $g.l^{-1}$ $Pd(NO_3)_2$ and 3 µl of 1.00 $g.l^{1}$ $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20°C. No certified value for bismuth and the amount of antimony was below the detection limits; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity (R^2 = 0.9997, 0.9998, and 0.9998 for Bi, Sb, and Se, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified values in Table 5. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 105, 97, and 101.5 % for Bi, Sb, and Se, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 5.

Pig Kidney from Institute for Reference Materials and Measurements (BCR-CRM 186)

The sample was diluted (about 1:29.5, v/v) with 0.2% HNO_3. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 $g.l^{-1}$ $Pd(NO_3)_2$ and 3 µl of 1.00 $g.l^{1}$ $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20°C. No certified values for bismuth and antimony; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity (R^2 = 0.9999, 0.9998, and 0.9995 for Bi, Sb, and Se, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified values in Table 5. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 99.6, 99.1, and 99.1 % for Bi, Sb, and Se, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 5.

Pork Liver from National Research Centre for Certified Reference Materials (GBW 08551)

The sample was diluted (about 1:4, v/v) with 0.2% HNO_3. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 $g.l^{-1}$ $Pd(NO_3)_2$ and 3 µl of 1.00 $g.l^{1}$ $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20°C. No certified values for bismuth and antimony; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity (R^2 = 0.9992, 0.9994, and 0.9992 for Bi, Sb, and Se, respectively) were used to determine the concentration of the elements in the sample. The results are summarized and compared with the certified concentrations in Table 5. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 100.9, 102.5, and 96.9 % for Bi, Sb, and Se, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 5.

Tea sample from National Research Centre for Certified Reference Materials (GBW 08505)

The sample was diluted (about 1:5, v/v) with 0.2% HNO_3. For each measurement, 20 µl of the diluted sample, 5 µl of 1.00 $g.l^{-1}$ $Pd(NO_3)_2$ and 3 µl of 1.00 $g.l^{1}$ $Mg(NO_2)_3$ modifier solution were injected into the graphite tube at 20°C. No certified values for these elements; therefore, the sample has been spiked with them before dilution.

The standard addition curves with good linearity (R^2 = 0.9995, 0.9996, and 0.9995 for Bi, Sb, and Se, respectively) were used to evaluate the concentration of the elements in the sample. The results are summarized and compared with the certified concentrations in Table 5. The experimentally determined concentrations were in good agreement with the certified values. The analyzed values were in the range of 101.4, 97.2, and 99.2 % for Bi, Sb, and Se, respectively. The detection limits (LOD) and the characteristic mass were determined and given in Table 5.

Table 5. The results of simultaneous determination of Bi, Sb, and Se

Sample		Bi	Sb	Se
Seronorm With Pd+Mg modifier	Con. Found (µg l^{-1})	20.5	94.4	60.8
	Con. Certified (µg l^{-1})	20.1	99.9	58.6
	DL (µg l^{-1})	0.82	0.67	1.5
	CM (pg)	80	48.9	146.7
	% RSD**	8.9	5.9	9.4
Seronorm With Ir modifier	Con. Found (µg l^{-1})	21.9	105.4	59
	Con. Certified (µg l^{-1})	20.1	99.9	58.6
	DL (µg l^{-1})	1.9	1.7	2.4
	CM (pg)	110	62.9	176
	% RSD**	10.5	7.4	6.0
Bio-Rad	Con. Found (µg l^{-1})	12.2	16.8	82.3
	Con. Certified (µg l^{-1})	12*	16.4	77
	DL (µg l^{-1})	0.82	0.75	1.3
	CM (pg)	80	73.3	125.7
	% RSD	3.0	2.4	2.3
Bovine Liver NIST 1577b	Con. Found (µg l^{-1})	10.5	9.7	7.6
	Con. Certified (µg l^{-1})	10*	10*	7.49
	DL (µg l^{-1})	1.2	1.4	1.5
	CM (pg)	88	58.7	88
	% RSD**	10.8	3.1	12.9
Pig Kidny BCR 186	Con. Found (µg l^{-1})	288.8	287.3	100.5
	Con. Certified (µg l^{-1})	290*	290*	101.4
	DL (µg l^{-1})	0.82	1.2	1.0
	CM (pg)	80	67.7	73.3
	% RSD**	6.7	3.0	16.7
Pork Liver GBW 8551	Con. Found (µg l^{-1})	40.36	41	9.23
	Con. Certified (µg l^{-1})	40*	40*	9.39
	DL (µg l^{-1})	1.1	1.1	1.2
	CM (pg)	80	55	67.7
	% RSD**	7.1	4.7	8.6
Tea GBW 8505	Con. Found (µg l^{-1})	50.7	48.6	49.6
	Con. Certified (µg l^{-1})	50*	50*	50*
	DL (µg l^{-1})	1.3	0.83	0.92
	CM (pg)	125.7	48.9	67.7
	% RSD**	8.8	6.0	4.9

* *Added*
** *For five replicates*

CONCLUSION

Simultaneous Multi-Element Atomic Absorption Spectrometer (SIMAA 6000) can be used to determine groups of elements (up to six) simultaneously, by using 2-operating and 4-operating modes, if the temperature program has been carefully optimized taking into account all analytes to be determined. A universal powerful matrix modifier should be used in order to increase the stability of the elements (especially the volatile elements). This will permit the use of a common temperature program including volatile and less volatile elements. All tested chemical modifiers increased the thermal stability of the elements. The Pd+Mg mixture modifier stabilizes the high and mid volatile elements. The stabilization effect appears in using higher pyrolysis temperature (up to 1000°C comparison with the situation without modifier) and to some extent the atomization temperature. Ir coating of the tube or

platform extend significantly the tube lifetime. Also, Ir coating is not time-consuming and so the proposed methodology is a useful analytical tool for routine analysis. The detection limits values of the multi-element determination were higher than those of the single-element which is mainly as a result of decreasing the lamp intensities in the multi-element mode compared to the single-element mode. Another effect which could cause the higher detection limits is the use of higher atomization temperature.

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